DYNAMIC MODEL OF CO_2 REMOVAL USING ASPEN HYSYS

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ABSTRAK

Objektif kajian ini adalah untuk merangsang proses penyingkiran CO_2 dengan menggunakan HYSYS Aspen. Metodologi kajian ini terbahagi kepada dua fasa. Fasa pertama adalah berkaitan dengan pembangunan model keadaan mantap dan fasa kedua yang berkaitan dengan simulasi dinamik. Dalam fasa pertama, reka bentuk data yang dikumpul daripada industri. Keputusan simulasi ini kemudiannya dibandingkan dengan data reka bentuk yang ada. Fasa kedua pada asasnya melibatkan peralatan saiz yang perlu dijalankan sebelum model dinamik maju. Pengesahan model dinamik dan data tumbuhan sebenar dipertimbangkan berdasarkan keadaan biasa. Simulasi tidak normal kemudian dijalankan dengan memperkenalkan gangguan dan atau kekurangan dalam proses. Sebagai kesimpulan, simulasi ini boleh digunakan sebagai latihan dan pembelajaran alat untuk jurutera dan pengendali, untuk memahami ciri-ciri dinamik proses penyingkiran CO_2 dan juga boleh menggunakan simulasi untuk prestasi yang lebih baik daripada proses penyingkiran CO_2.

ABSTRACT

The objective if this study is to stimulate CO_2 removal process by using Aspen HYSYS. The methodology of this study is divided into two phase. The first phase relates to the model development of steady state and the second phase related to dynamic simulation. In the first phase, the design data are collected from an industry. The simulation results are then compared to the available design data. The second phase basically involves equipment sizing that should be conducted before the dynamic modeling is developed. Validation of dynamic model and real plant data is considered based on normal condition. The abnormal simulation is then conducted by introducing disturbances and or faults in the process. As the conclusion, this simulation can be used as training and learning tools for engineers and operator, to understand the dynamic characteristic of CO_2 removal process and also be able to use the simulation to improved performance of the CO_2 removal process.

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LIST OF SYMBOLS

%	percentage
kPa	kilopascal
psi	pounds per square inch pressure
°C	degree celcius
kg	kilogram
m^3	volume

LIST OF ABBREVIATIONS

CO	Carbon monoxide
CO_2	Carbon dioxide
DEA	Diethanolamine
DGA	Diglycolamine
DIPA	Diisopropanolamine
CH4	Methane
H2	Hydrogen
H2S	Hydrogen Sulphide
MDEA	Methylethanolamine
MEA	Monoethanol amine
N2	Nitrogen
H2O	Water

CHAPTER 1

1.0 INTRODUCTION

1.1 Background of Proposed Study

The process of carbon dioxide removal starts from the absorber which the lean amine enter upper steam to the absorber whereas the natural gas enter from lower of the absorber. The reaction occurs and amine absorbs carbon dioxide from natural gas which is called rich amine. Rich amine then transfer to the stripper which released the carbon dioxide from amine. Then amine is feedback to absorber, and used all over again. Almost all industries that involve natural gas as a raw material must go through CO_2 removal process before proceeding to further process of natural gas. The amount of carbon dioxide contents in the natural gas can vary from 4% to 50% depending on the gas source. Before the transportation of natural gas, it must be pre-processed in order to meet the typical pipeline specification of 2–5% carbon dioxide. Aspen Hysys has been used since 2000 to simulate CO_2 removal from gas based power plants. Aspen Hysys is use in order to calculate permeate and retentate of the system with any number of modules, allowing complex process simulations. The programme has the possibility to use ASPEN HYSYS capabilities to calculate mass and energy balances and combine in the process model. The important process parameters are flow rates, temperatures,

compositions, pressure ratio (between the upstream pressure and downstream pressure over the membrane) and stage cut (ratio of permeate to feed flow rate).

1.2 Problem Statement

When an abnormal occurs and we want to find the source of the problem, to do trial and error to the real plant will cause harmful to the workers, effect the purity of the product and also lost time, energy and material.

1.3 Research Objective

1.3.1 To develop dynamic simulation using Aspen HYSYS.

1.3.2 To understand the characteristics of CO_2 removal.

1.3.3 To control the dynamic simulation of CO_2 removal.

1.3.4 To improve the performance of CO_2 removal.

1.4 Research Questions

1.4.1 How to develop dynamic simulation?

1.4.2 Can the performance of CO_2 removal be improved by using dynamic simulation?

1.5 Scope of Proposed Study

The scope of the study is the CO_2 removal by amine absorption from a gas based power plant and also simulation using Aspen HYSYS or Aspen Plus.

1.6 Expected Outcomes

The expected outcomes for this proposed study are to use simulation as training and learning tools for engineers and operator, to understand the dynamic characteristic of CO_2 removal process and also be able to use the simulation to improved performance of the CO_2 removal process.

1.7 Significance of Proposed Study

The training and learning simulation of CO_2 removal can be developed and to become the bench mark for the CO_2 removal industries.

1.8 Conclusion

Dynamic simulation uses software in order to make a process that can be used in a bigger plant and also can be used to improve the process without disturbing the real process. Software process simulation modeling is beginning to be used to address a variety of issues from the strategic management of software development, to supporting process improvements, to software project management training. As a conclusion, dynamic simulation gave a lot of benefits to human to make life easier.

CHAPTER 2

2.0 LITERATURE REVIEW

2.1 Introduction

The research is about dynamic simulation of carbon dioxide removal using Aspen HYSYS. Aspen HYSYS is a computer program that simulates chemical processes. Using a computer for a process simulation takes a fraction of the time it takes to do it by hand. The speed of a computer simulation allows the user to observe quickly the effect of changes in a simulation. For example, using HYSYS, it easily compares the amount of product produced using different ratios of starting materials. Doing this comparison with hand calculation would be a long and tedious task. The objective of this research is to develop the dynamic simulation of carbon dioxide removal by control, operational management, process improvement, technology adoption, understanding, training and learning.

2.2 Carbon Dioxide Removal Process

Gas sweeting process often referred to the removal of acid gases (CO_2, H_2S and other sulfur components) from natural gas. Carbon dioxide present in the natural gas

need to be removed in other to; increase the heating value of the gas, prevent corrosion of pipeline and gas process equipment and crystallization of CO_2 during cryogenic process (liquefaction process). The removal of carbon dioxide can be accomplished in a numbers of ways. Varieties of processes and (improvement of each) have been developed over the years to treat certain types of gas with the aim of optimizing capital cost and operating cost, meet Gas specifications and for environmental purpose (Tennyson et .al 1977). The major processes available can be grouped as follows (Maddox, 1982);

- Absorption Processes (Chemical and Physical absorption)
- Adsorption Process (Solid Surface)

The flow diagram of CO_2 removal simulation of amine process is shown in Figure 2.1. The natural gas is feed into the absorber than the CO_2 in the natural gas is absorbed by lean amine. Natural gas without CO_2 is then use for further process. The focusing process is CO_2 removal which happens in two processes which is absorber and stripper. In the absorber, the natural gas is feed from lower part of the absorber then the lean amine (amine without CO_2) is feed from upper side of the absorber. Then the absorption occurs between natural gas and amine. Amine absorbs CO_2 that carry by natural gas then amine leave the absorber carrying CO_2. The rich amine (amine with CO_2) then move to the stripper where the CO_2 is removes from amine. Then from rich amine, it becomes lean amine which is used over again for removing CO_2 in the absorber.

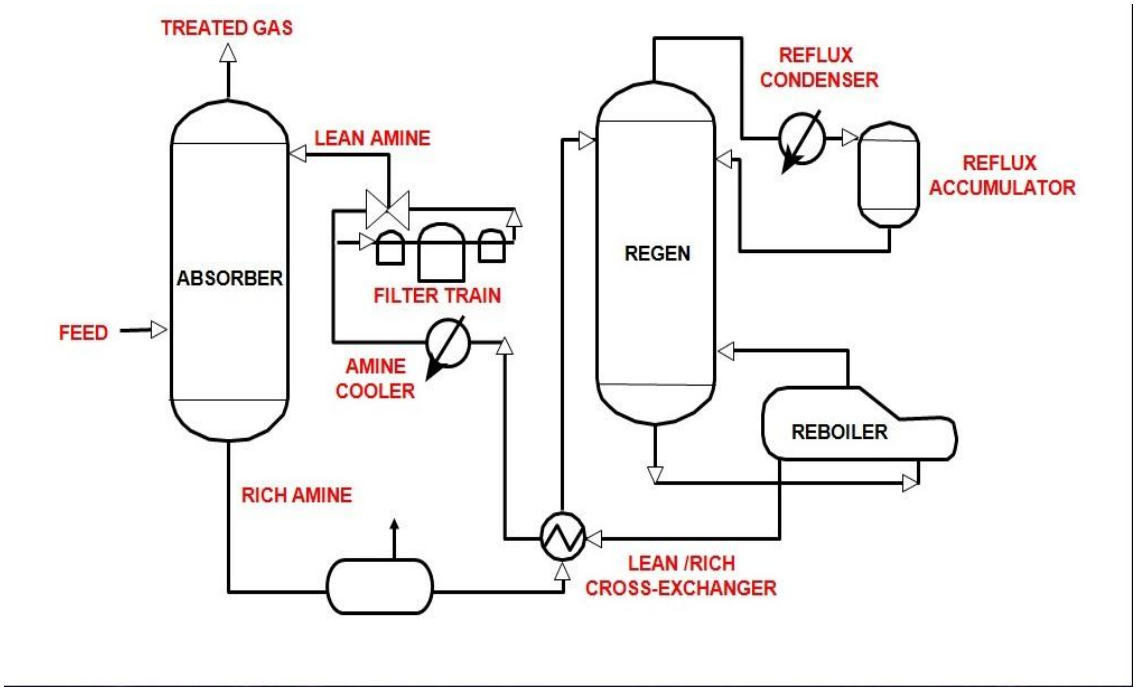

Figure 2.1: The flow diagram of CO_2 removal simulation of amine process

An absorption and desorption process for CO_2 removal with an aqueous MDEA solution had been simulated. The exhaust gas from the power plant model is used as the feed to this model. The absorption column is specified with 30 stages each with a Murphree efficiency of 0.25. (An estimated HETP (Height Equivalent to a Theoretical plate) of 4 meter, is about equivalent to 0.25 efficiency for each meter of packing.) Traditional concentrations, temperatures and pressures are used in the base case simulation. The thermodynamics for this mixture is described by an Amines Property Package available in Aspen HYSYS. The Kent Eisenberg [10] model is selected in the Amines Property Package. Specifications for the calculation are listed in table 2. The Aspen HYSYS CO_2 removal model is presented in figure 5. Different versions of this model have been developed in several student projects. The version in figure 5 is based on a Master Project work by Trine Amundsen. (Amundsen, T., 2007).

Table 1: Data from industry

Inlet gas temperature	46°C
Inlet gas pressure	674.7 kPa
Inlet gas flow	58934 Kg/hr
CO2 in inlet gas	0.10 mole %
Water in inlet gas	0.015 mole %
Lean amine temperature	60°C
Lean amine pressure	655.1 kPa
Lean amine rate	5088.39 kgmole/hr
MDEA content in lean amine	0.96 mole %
CO2 in lean amine	0.036 mole %
Number of stages in absorber	30

2.2.1 Physical Absorption Processes

Physical solvent processes use organic solvents to physically absorb acid gas components rather than react chemically. Physical absorption processes of removing CO_2 are based on the solubility of CO_2 within the solvents. CO_2 solubility depends on the partial pressure and on the temperature of the feed gas. Higher CO_2 partial pressure and lower temperature favors the solubility of CO_2 in the solvents as absorbent, at these conditions complete removal of acid gas from natural gas is possible. Regeneration of the spent solvent can be achieved by flashing to lower pressure or by stripping with vapor or inert gas, while some is regenerated by flashing only and require no heat (Dimethyl ether of Polyethylene Glycol).

Selection of physical processes for the removal of CO_2 from natural gas is favored on the following conditions;

i. The partial pressure of the CO_2 in the feed should be 50 psi or higher

ii. The concentration of heavy hydrocarbon in the feed should be low.

iii. Only bulk removal of acid gas is required.

iv. Selective removal of CO_2 is required.

2.2.2 Chemical Absorption Process

Chemical absorption processes are based on the exothermic reaction of the solvent to remove the CO_2 that present in the gas stream. In this case, reactive material (solvent) remove CO_2 in the contactor at high pressure and preferably at low temperature and most chemical reaction are reversible. The reaction is then reversed by endothermic reaction using the stripping process at high temperature and low pressure. Chemical absorption processes are particularly applicable where acid gas (CO_2) partial pressure are low and for low level of acid gas requirement in the residue gas. The solvent more suitable for feed sour gas rich in heavy hydrocarbon because of the water content of the solution minimize the heavy hydrocarbon absorption. Most of chemical solvent processes use either an amine or carbonate solution.

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2.3 Amine Base Process Facilities

The alkanolamines are generally accepted and widely used of the various available solvents for removal of CO_2 from natural gas stream (Bottom, 1930). Monoethanolamine (MDEA) and Diethanolamone (DEA) have made the solvent achieved a pinnacle position in the gas processing industry because of their reactivity and availability at low cost especially.

Formation of carbonate bicarbonate:

$$2RNH_2 + H_2O + CO_2 \Leftrightarrow (RNH_3)_2CO_3 \qquad (2.1)$$

$$(RNH_3)_2CO_3 + H_2O + CO_2 \Leftrightarrow 2RNH_3HCO_3 \qquad (2.2)$$

Formation of carbamate:

$$2RNH_2 + CO_2 \Leftrightarrow RNHCOONH_3R \qquad (2.3)$$

The reactions above shown the reaction proceed to the right at low temperature and to the left at a higher temperature, thus making CO_2 to be absorbed at ambient temperature. The reaction is reversed that is backward reaction is favored at elevated temperature (as obtained in the stripper column) where the carbonate salt formed is decomposed to release the acid gas absorbed, therefore stringent control of stripper column temperature should be adopted to reduce the release of carbonate salt. Reaction (2.1) and (2.2) are slow reaction because carbon dioxide must form carbonic acid with water (slow reaction) before reacting with amine. Elimination of selectivity of hydrogen sulfide is impossible because of reaction (2.3) which predominate when MEA is involved is relatively fast. Methyldiethanolamine (MDEA) and diethanolamine (DEA) are today the most tertiary amines for acid gas removal (Rejoy et.al., 1997).

Diglycoamine, diisopropanaolamine and methyldiethanolamine are other amine solutions that can be used for this purpose.

Monoethanolamine (MEA**);** the concentration of MEA in solution is usually about 10-15% by weight. MEA is very reactive and can absorbed CO_2 and H_2S simultaneously. MEA however react with COS, CS_2 and mercaptans. Its relatively high vapour pressure Cause greater losses compared with other amine. For this reason it is use for intensive purification, with fairly low H_2S concentrations for a gas containing no COS or CS_2.

Diethanolamine(DEA) helps to overcome the limitation of MEA, and can be used in the present of COS and CS_2. The application of DEA to natural gas processing was described by Berthier in 1959 (Kohl and Riesenfeld, 1985). Operating with solutions containing 25-30% by weight of DEA can be used to process Natural gas with even High acid gases contents.

Diglycolamine(DGA) exhibit similar properties with monoethanolamine, but is less volatile, and therefore be used in much higher concentration (40 – 60%). This helps to reduce the circulation rate, thus increase the economics of the process.

Diisopropanolamine(DIPA) is used, in relatively high concentration from (30 – 40%) by the "Adip Process (Shell International Petroleum Company) (Klein, 1970). This solution is mostly use in processing of refinery gas or liquid with high COS.

Methylethanolamine(MDEA) allows the selective absorption of H_2S in the presence of CO_2, but can be used effectively to remove CO_2 from natural gas in present of additives (Meisner and wager, 1983).The reaction between CO_2 and MDEA solution is presented as follow;

$CO_2 + MDEA + H_2O \Leftrightarrow HCO_3^- + MDEA^+$ **(2.4)**

The normal range of acid gas pickup, mol/ mol of amine (MDEA) is from 0.2 – 0.55(Perry, 1974).

Amine solutions are basic and hence non-corrosive but they are sometime use as corrosion inhibitors. Significant corrosion may occur at points where the concentration and temperature of acid gas is high in the presence of acid gases. The application of primary solution requires the use of corrosion inhibitors and the unit may be made of special steels because primary amines are the most corrosive (DuPart et al., 1993). Foaming is a frequent problem in these installations due the following;

• Suspended solids

• Condensed hydrocarbon

• Amine-degradation products.

• Foreign matter from corrosion inhibitors.

The foaming tendency in these installations can be prevented by good design and operation; also anti-foaming agents can be used (Kohl and Riesenfeld, 1985). Filtration of the solvent recycled to the absorber step is essentially important. The recommended filter that will retain particle sizes is larger than 10μm (Pauley et al., 1989). Degradation of amine solvents occur when get in contact with the air or oxygen, and the oxidation products often cause corrosion. Oxidation can be reduced by placing the amine solutions under an inert gas blanket in the storage tanks.

2.4 Absorption and Reaction Mechanisms

The details of the mechanisms of CO_2 absorption into an amine solution in an absorption column are complicated. There are a lot of references about the chemistry involved in the process, and many references and models comprising mass transfer mechanisms and chemical reaction kinetics. The first step is CO_2 has to be transported from the gas to the liquid surface, and then it is absorbed in the liquid solution. The gas liquid interface area a (in m^2/m^3) and liquid holdup h (in m^3/m^3) are main parameters in describing such mechanisms. The CO_2 may react chemically with other components in the liquid.

The following reactions are assumed to take place when CO_2 reacts in a primary amine like MEA (monoethylamine) in an aqueous solution. In the case of MEA ($NH_2C_2H_2OH$), R is C_2H_2OH.

$$CO_2 + NRH_2 \rightarrow RH_2^+NCOO^{--} \qquad (2.5)$$

$$RH_2^+NCOO^{--} + NRH_2 \rightarrow RH_2NCOO^{--}NRH_2^+ \qquad (2.6)$$

According to equation (2.5) and (2.6), two moles of MEA are necessary to absorb one mole of CO_2. A simple overall description of the combined absorption and reaction process is simply

$$CO_2 \text{ (gas)} \rightarrow CO_2 \text{ (absorbed)} \qquad (2.7)$$

The CO_2 is not 100 % removed from the gas. The percentage of CO_2 removal is limited both by low absorption and reaction rates and also by the equilibrium conditions. If the kinetics in the reactions should be calculated, more details about the intermediate reactions in equation (2.5) and (2.6) should be included. This is done in the MEA property insert model in Aspen Plus. The simulation program Aspen HYSYS is mainly

based on equilibrium calculations. In that case, equation (2.7) is sufficient to calculate the absorption process. (Lars Erik, 2007).

2.5 Simulation Using Aspen HYSYS

The commercial process simulation tools such as ProVision, ProMax or Aspen Plus can also be used to simulate the process as Aspen HYSYS. Aspen Plus has the possibility to calculate rate expressions on an ideal mixing stage (simulating a column plate). This has the advantage of taking into account the reaction rates for different reactions simultaneously. It is possible to include rate expressions of absorption (transport of CO_2 from the gas to the liquid phase) in such a model but it is difficult to be done. It is also a question whether this kind of a mixing stage model is a good model for continuous countercurrent operation as in structured packing. On the other hand, the presented Aspen HYSYS model is based on a specified Murphree efficiency for each stage (or height of packing). It is possible to make this efficiency a function of rate expressions for the absorption rate and the reaction rates. It is of course possible to simulate CO_2 removal processes without using commercial process simulation programs. It is however necessary to include at least one reliable and robust equilibrium calculation model and one robust column model. It is difficult to compete with the commercial process simulation programs in these two matters. The commercial programs also normally have very good input and output facilities. A problem with the commercial process simulation programs, at least from an academic point of view, is that some of the models of interest are not documented accurately. (Lars Erik, 2007).